Heavy metals in fish (*Solea vulgaris*, *Anguilla anguilla* and *Liza aurata*) from salt marshes on the southern Atlantic coast of Spain

José Usero, Carmen Izquierdo, José Morillo*, Ignacio Gracia

Department of Chemical and Environmental Engineering, School of Engineers, University of Seville, Camino de los Descubrimientos s/n, 41092 Seville, Spain

Received 20 December 2002; accepted 3 March 2003

Abstract

Comparisons were made of metal concentrations in water and sediment with those in the muscle and livers of three species of fish caught in four seawater reservoirs (two in the Odiel estuary and two in the Bay of Cádiz). The concentrations of a large number of metals in the water, sediment and fish were higher in the Odiel reservoirs than in those in Cádiz. We found high metal-enrichment factors in the livers as compared to muscle (over 100 for Fe and Cu and around 5 for Zn, Ni, Cd and Pb). The three fish species showed differences in metal content. For example, eels accumulated more metals in muscle and grey mullet in the liver. The metal levels found in muscle in the three species were below the legal limits for human consumption, although Cu in the liver was above the limit in the three species taken from the Odiel reservoirs, and Zn levels in liver were over the maximum in eels from one of the Odiel marshes. Significant correlations (*p* < 0.05) were obtained for the levels of numerous metals in water, sediment and fish.

© 2003 Elsevier Science Ltd. All rights reserved.

Keywords: Metal pollution; Water; Sediment; Fish

1. Introduction

Spain is, after Japan, the world’s second fish-consuming country, at over 30 kg per person per year, and consumption is expected to rise in the future.

The Spanish fishing fleet is going through a lengthy, profound crisis, brought about by overfishing in the country’s fishing grounds and the increasing limitations being imposed by most of the countries where Spain’s fleet has traditionally fished.

Because of this situation, there is currently a great deal of interest in supplementing fishing with production activities (aquaculture)—i.e., moving from simply catching aquatic species to breeding those best suited to human consumption. In recent years, aquaculture has been growing rapidly in the salt marshes on the southern Spanish Atlantic coast. Seawater reservoirs are created by enclosing a portion of the salt marsh to guarantee a constant supply of water for the saltworks. This then becomes available for what is known as “extensive” aquaculture, in which large amounts of natural water are used with little or no change in the environment in which the fish are raised.

The fry enter the seawater reservoirs from the sea, attracted by the greater abundance of food. When a sufficient number of fry have entered, sluicegates keep them from getting out until they have attained the proper size for catching. This extensive model gives low yields but costs are very low both for investment (it uses the existing saltworks facilities) and operation (it is not necessary to feed the fish).

Fish are a major part of the human diet and it is therefore not surprising that numerous studies have been carried out on metal pollution in different species of edible fish (Kucuksezgin et al., 2001; Lewis et al., 2002; Prudente et al., 1997). Much has also been written about metal levels as a whole in fish, water and sediment in particular areas (Sánchez et al., 1998; Guhathakurta and Kaviraj, 2000; Topçuoglu et al., 2002; Karade of and Ünlü, 2000). A problem that may arise in these papers is that, given the mobility of fish, the individuals caught in one place may come from a distant geographic area (especially in the case of marine fish). Likewise, studies...
carried out in large aquariums cannot be considered representative of a natural environment since, for example, the fish receive food coming from outside and the studies usually cover a relatively short period of time (a few months or weeks).

This study analyses and compares metal concentrations in water, sediment and three fish species from four large seawater reservoirs where extensive aquaculture is practised. It is therefore safe to say that the fish have spent most of their lives in this environment and have not received food from outside or any other type of external influence. The metal content in the dorsal muscle was analysed in each species because of its importance for human consumption, and the liver was also analysed since this organ tends to accumulate metals (Marcovecchio et al., 1991). It is also a good indicator of chronic exposure to heavy metals because it is the site of metal metabolism (Miller et al., 1992).

The reservoirs studied are located in two areas (Odiel and Cádiz) with different metal-pollution levels (Fig. 1). The reservoirs selected in the Odiel area (Bacuta and Liebre) are affected by the Odiel River, which flows through a well-known mining area, the Iberian Pyrite Belt (Leblanc et al., 2000). There are far fewer sources of metal pollution in the Cádiz reservoirs (San Juan and San Carlos). The four reservoirs chosen are irregularly shaped and each has an area of approximately 125,000 m², except the Liebre reservoir, which has an area of 250,000 m².

Finally, the metal-pollution levels of three species studied—common sole (Solea vulgaris), eel (Anguilla anguilla) and grey mullet (Liza aurata)—were used as the basis to determine whether they are suitable for human consumption.

2. Materials and methods

2.1. Fish

Large-scale fishing using nets takes place once a year in the selected seawater reservoirs (Fig. 1), which means that all the fish caught are approximately the same age. We took advantage of this to choose 10 fish of each species from each reservoir. From each of these groups of 10 fish, we made a compound sample of dorsal muscle and another of liver, for a total of 12 muscle samples (3 species and 4 reservoirs) and 12 liver samples. All 24 samples were freeze-dried and crushed to uniform particle size before analysis (Miao et al., 2001). The resulting powder then underwent acid digestion (HNO₃ – H₂O₂) in an automatic microwave digestion system (Kingston and Jassie, 1988). In recent years, microwave digestion procedures have been used in numerous studies (Lewis et al., 2002; Kucuksezgin et al., 2001; Karadede and Ünlü, 2000) owing to the advantages of this technique, which include speed of digestion and less possibility of contamination during the process (Sures et al., 1995).

Following acid digestion, all the samples were analysed for 10 elements by atomic absorption spectrometry (AAS). Fe, Zn, and Mn were determined in an air-acetylene flame (Perkin-Elmer 2380 with double beam and deuterium background corrector). Cu, Cd, Cr, Ni, and Pb were analysed in a graphite furnace (Perkin-Elmer 4110 ZL with Zeeman background corrector) with an autosampler. The standard addition method was used to correct for matrix effects. Cold-vapour and hydride-generation techniques were used for analysis of Hg and As, respectively.

2.2. Sediment

Core samples up to 20 cm in length were taken from 16 sampling sites (four sampling sites in each one of the four reservoirs selected) using polyvinyl chloride (PVC) corers (Cabrera et al., 1992). The corers were immediately sealed and stored at 4 °C until arriving at the laboratory.

In the laboratory, the cores were extruded and sectioned. The first 5-cm section of each core was used in this study (Meyerson et al., 1981). Sections were air-dried (Thomas et al., 1994; Friedler et al., 1994) and sieved with a 63-µm nylon mesh, and the fraction <63 µm was chosen for chemical analysis (Salomons and Förstner, 1984; Rauret et al., 1988; Thomas et al., 1994). The samples underwent acid digestion (HNO₃ – HCLO₄) in an automatic microwave digestion system and their metal content was analysed by AAS.
2.3. Water

Water samples were taken from the same sampling sites as the sediment, using 1-l acid-leached polyethylene bottles. The samples collected were filtered through a 0.45-μm membrane filter, acidified with 2 ml of concentrated HNO₃ and stored at room temperature until analysis. The samples were analysed by graphite furnace AAS, with Zeeman background corrector, after preliminary metal concentration according to the method described by Sturgeon et al. (1980), except for Hg and As, which were analysed respectively by cold vapour and hydride generation.

2.4. Reagents and quality assurance

All reagents used were of analytical grade (Merck). Standard working solutions of the different elements analysed were prepared from the corresponding 1000 mg/l Merck Titrisol solution.

The digestion and analytical procedures were checked by analysis of standard reference materials (sediment: CRM-277, Community Bureau of Reference; fish: DORM-2, National Research Council; and seawater: CASS-3, National Research Council Canada). Replicate analysis of these reference materials showed good accuracy, with recovery rates for metals between 88% and 104% for fish, 92% and 98% for sediment and between 95% and 102% for water.

3. Results and discussion

3.1. Sediment

The highest concentration levels of most of the metals analysed (Table 1) were found in the sediment from the Odiel seawater reservoirs (Bacuta and Liebre). We must bear in mind that these reservoirs are affected by pollutants from the Odiel River, which, as previously mentioned, flows through a mining area (Iberian Pyrite Belt).

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Mean concentrations (mg/kg dry mass) of heavy metals in sediment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal</td>
<td>Odiel seawater reservoirs</td>
</tr>
<tr>
<td></td>
<td>Bacuta</td>
</tr>
<tr>
<td>As</td>
<td>81 ± 4</td>
</tr>
<tr>
<td>Hg</td>
<td>0.7 ± 0.1</td>
</tr>
<tr>
<td>Mn</td>
<td>563 ± 50</td>
</tr>
<tr>
<td>Zn</td>
<td>1000 ± 50</td>
</tr>
<tr>
<td>Fe</td>
<td>40,200 ± 2200</td>
</tr>
<tr>
<td>Cu</td>
<td>221 ± 21</td>
</tr>
<tr>
<td>Ni</td>
<td>46 ± 3</td>
</tr>
<tr>
<td>Cd</td>
<td>9 ± 1</td>
</tr>
<tr>
<td>Pb</td>
<td>116 ± 10</td>
</tr>
<tr>
<td>Cr</td>
<td>67 ± 4</td>
</tr>
</tbody>
</table>

Mean ± standard deviation (four sampling sites).

Iron is the most abundant metal in all of the reservoirs because it is one of the most common elements in the earth’s crust and the sediment from the Odiel reservoirs has a high pyrite (FeS₂) content. According to Cabrera et al. (1999), pyrite oxidation produces sulphate and the Fe²⁺ ion, which is oxidised to Fe³⁺ by microorganisms such as Thiobacillus ferrooxidans.

High concentrations of As, Zn, Pb, Cu and Cd were found in the sediment from the Odiel reservoirs and were comparable only to those found in other areas affected by pyrite pollution, such as the Huelva estuary (Pérez et al., 1991) and the Tinto River (Morillo et al., 2002; Elbaz Poulichet et al., 2001), or because of significant industrial dumping as in Gdansk Bay en Poland (Glasby and Szefer, 1998). On the contrary, in the Bay of Cádiz reservoirs, the levels of these metals were low, similar to those found in sediment from other non-polluted areas (Forstner and Wittman, 1983). An exception to this was Pb, which reached considerably higher concentrations (61 ± 6 mg/kg) in the San Juan reservoir than in San Carlos (26 ± 2 mg/kg). This is because the San Juan reservoir is near a heavily travelled highway.

On the other hand, no noteworthy differences were found in the Cr and Mn concentrations among the four seawater reservoirs studied. The levels of these metals were similar to those obtained by other authors in non-polluted sediment in the area (Ruiz, 2001; Usero et al., 2000).

3.2. Water

As with the sediment, the highest metal concentrations were found in the Odiel reservoirs (Table 2). The only exception to the foregoing was Pb, which attained its highest level in the water from the San Juan reservoir (1.3 μg/l). Bearing in mind the absence of industrial dumping of Pb in the area, this may be due to a heavily travelled road that runs along the reservoir. Higher levels of Pb often occur in water bodies near highways and large cities due to high gasoline combustion (Banat et al., 1998). The Pb concentration in this reservoir was similar to that found by Bravo-Sánchez et al. (2001) at points close to the city of Avilés on the coast of Asturias (Spain).

The highest mean concentrations of As (60 μg/l), Zn (57 μg/l), Cu (11 μg/l), Fe (32 μg/l) and Cd (3.4 μg/l) were found in the Liebre reservoir, followed by Bacuta. These concentrations were considerably higher than those usually found in the scientific literature on seawater (Millward et al., 1998; Achterberg et al., 1999; Nicolai et al., 1999; Côtte-Krief et al., 2000). On the contrary, the Cádiz reservoirs showed As, Zn, Cu, Fe and Cd concentrations that were comparable to, or slightly higher than, those reported in other studies for coastal and estuary waters. For example, the mean As levels of 1.3 and 1.5 μg/l in these reservoirs (San Juan and San Carlos, respectively) are similar to those reported by Munksgaard and Parry (2001) in Port Darwin (north Australian coast). Work done by Morales et al. (1999)
in the Gulf of Valencia and by Banat et al. (1998) on the
coast of the United Arab Emirates show Cd and Zn levels
similar to those of the Cádiz reservoirs. Cu concentrations
(1.6 μg/l in San Carlos and 2.2 μl/l in San Juan) were of the
same order of magnitude as those found by Nicolai et al.
(1999) in the Rhone River estuary in France. The Andalusian
Regional Ministry of the Environment (C.M.A., 2001)
obtained a mean iron concentration of 14 mg/l in coastal
waters of the Spanish southwest, similar to the levels found
at the mouth of the Odiel River (Basque Country, Spain)
polluted by mining activities, Sañchez et al. (1998) found a Cu concentration of
34 mg/kg in eel livers and 185 mg/kg in those of brown
tROUT. Fe concentrations similar to those of the Odiel
reservoirs were found in the livers of grey mullets from
the Huelva estuary (AIQB, 2001), an area polluted by
industrial and mining effluents.

Table 3

<table>
<thead>
<tr>
<th>Metal</th>
<th>Grey mullet (Liza aurata)</th>
<th>Eel (Anguilla anguilla)</th>
<th>Common sole (Solea vulgaris)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bacuta</td>
<td>Liebre</td>
<td>San Carlos</td>
</tr>
<tr>
<td>As</td>
<td>1.21</td>
<td>1.68</td>
<td>0.83</td>
</tr>
<tr>
<td>Hg</td>
<td>0.012</td>
<td>0.042</td>
<td>0.035</td>
</tr>
<tr>
<td>Mn</td>
<td>4.61</td>
<td>3.52</td>
<td>1.23</td>
</tr>
<tr>
<td>Zn</td>
<td>49.6</td>
<td>81.8</td>
<td>38.4</td>
</tr>
<tr>
<td>Fe</td>
<td>337</td>
<td>397</td>
<td>199</td>
</tr>
<tr>
<td>Cu</td>
<td>88.9</td>
<td>164</td>
<td>17.0</td>
</tr>
<tr>
<td>Ni</td>
<td>0.02</td>
<td>0.039</td>
<td>0.13</td>
</tr>
<tr>
<td>Cd</td>
<td>0.051</td>
<td>0.051</td>
<td>0.14</td>
</tr>
<tr>
<td>Pb</td>
<td>0.02</td>
<td>0.048</td>
<td>0.29</td>
</tr>
<tr>
<td>Cr</td>
<td>0.012</td>
<td>0.011</td>
<td>0.029</td>
</tr>
</tbody>
</table>

3.3. Fish

The concentrations of the metals analysed in the livers
and muscle of the three fish species are given in Tables 3
and 4, and Fig. 2 shows the mean metal concentrations in
the fish from each of the four reservoirs.

If we look first at the livers, we can say that fish in the
Odiel reservoirs (Liebre and Bacuta) had considerably
higher mean metal concentrations than fish from the Cádiz
reservoirs (San Carlos and San Juan), with the exception of Hg and Cr, probably because the levels of
these two elements showed scant differences between the
water and the sediment of the two areas studied (Odiel
and Cádiz). Among the Odiel reservoirs, the Liebre
reservoir showed the highest mean concentrations of Fe
(428 mg/kg), Cu (108 mg/kg), Zn (50.7 mg/kg), As (1.48
mg/kg), Pb (0.47 mg/kg), Cd (0.42 mg/kg) and Ni (0.24
mg/kg). It is to be noted that this reservoir presented the
highest pollution in water and sediment. The metal con-
centrations in the livers of the three species caught in the
Liebre reservoir were comparable to those of other studies
carried out in polluted areas. For example, the livers of
different species of fish in Bouillac (France), an area of the
Lot River polluted by effluents from a Zn mineral-
processing plant presented Zn levels around 50 mg/kg
(Andrés et al., 2000). In fish caught off the coast of the
United Arab Emirates (UAE) in the Arabian Gulf, an area
polluted by hydrocarbons and heavy metals, levels of Zn
(34–70 mg/kg) and Cd (0.51–0.63 mg/kg) similar to
those in our study were also found (Al-Yousuf et al.,
2000). In a study carried out in fish from the Urumea
River (Basque Country, Spain) polluted by mining activ-
ities, Sánchez et al. (1998) found a Cu concentration of
34 mg/kg in eel livers and 185 mg/kg in those of brown
tROUT. Fe concentrations similar to those of the Odiel
reservoirs were found in the livers of grey mullets from
the Huelva estuary (AIQB, 2001), an area polluted by
industrial and mining effluents.
Metal concentrations in the livers of fish from the Cádiz seawater reservoirs were similar to those reported by Blasco et al. (1998) in five species caught in other Cádiz reservoirs, with the exception of Zn, whose mean concentration (28 mg/kg) was lower than that reported by Blasco et al. (1998).

On the other hand, the metal levels in livers from the Cádiz seawater reservoirs were higher than those in fish from the Atatürk Dam Lake (Euphrates) in Turkey (Karadede and Ünlü, 2000), a non-polluted area.

With regard to muscle, we note first that metal concentrations in this part of fishes’ bodies were considerably lower than those found in the livers, as shown in Fig. 2 (mentioned above) and Fig. 3, which shows the enrichment factors in livers. These factors were calculated for each metal as the ratio of liver-to-muscle concentration. The accumulation of metals in the liver could be due to the greater tendency of the elements to react with the oxygen carboxylate, amino group, nitrogen and/or sulphur of the mercapto group in the metallothionein protein, whose concentration is highest in the liver (Al-Yousuf et al., 2000). The highest enrichment factors were obtained for Cu and Fe and were greater than 60. These results are in agreement with those reported in numerous studies (Allen-Gil et al., 1997; Mormede and Davies, 2001; Moissenko and Kudryavtseva, 2001). The haeompoietic function of the liver and the organ’s abundant blood supply explain the accumulation of Fe (Blasco et al., 1998). The accumulation of Cu can be explained by its relation to low-molecular-weight proteins (metallothionein-like), which are concentrated in hepatic tissue (Hamza-Chaffai et al., 1996; Ayas and Kolankaya, 1996). Significant enrichment with Zn, Ni, Cd and Pb was also found in the liver, with factors greater than 4. The lowest factors were obtained for Mn, As and Cr (less than 1). In other words, the Mn, As and Cr concentrations—as opposed to the other elements—were higher in muscle than in liver. For most of the metals analysed, maximum enrichment factors were found in the Liebre reservoir (the most polluted), from which it can be deduced that environmental pollution affects the liver more than muscle.

Similarly to what we have said in relation to the livers, the mean metal concentrations in muscle from fish in the Odiel seawater reservoirs were higher than those found in fish from the Cádiz reservoirs (see Fig. 2), although the

![Fig. 2. Mean metal concentrations in the four reservoirs studied (mg/kg wet mass).](image)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Grey mullet (Liza aurata)</th>
<th>Eel (Anguilla anguilla)</th>
<th>Common sole (Solea vulgaris)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bacuta</td>
<td>Liebre</td>
<td>San Carlos</td>
<td>San Juan</td>
</tr>
<tr>
<td>As</td>
<td>1.98</td>
<td>2.00</td>
<td>1.36</td>
</tr>
<tr>
<td>Hg</td>
<td>0.013</td>
<td>0.013</td>
<td>0.010</td>
</tr>
<tr>
<td>Mn</td>
<td>2.33</td>
<td>2.45</td>
<td>2.50</td>
</tr>
<tr>
<td>Zn</td>
<td>6.07</td>
<td>8.41</td>
<td>3.87</td>
</tr>
<tr>
<td>Fe</td>
<td>5.40</td>
<td>7.13</td>
<td>4.11</td>
</tr>
<tr>
<td>Cu</td>
<td>0.5</td>
<td>0.6</td>
<td>0.2</td>
</tr>
<tr>
<td>Ni</td>
<td>0.070</td>
<td>0.024</td>
<td>0.021</td>
</tr>
<tr>
<td>Cd</td>
<td>0.030</td>
<td>0.021</td>
<td>0.013</td>
</tr>
<tr>
<td>Pb</td>
<td>0.03</td>
<td>0.03</td>
<td>0.04</td>
</tr>
<tr>
<td>Cr</td>
<td>0.038</td>
<td>0.032</td>
<td>0.029</td>
</tr>
</tbody>
</table>

![Fig. 3. Enrichment factors (metal concentration in liver/metal concentration in muscle) in the four reservoirs studied.](image)
differences were not as pronounced as with the livers. The greatest differences were seen for As and Mn, with mean values of 2.8 and 7.3 mg/kg in the Odiel and 1.6 and 3.1 mg/kg in the Cádiz reservoirs, respectively.

Fig. 2 also shows that Zn was the metal that reached the highest concentrations in muscle (between 6.05 mg/kg in San Juan and 9.31 mg/kg in Liebre). A high level of Zn in comparison to other elements is typical of fish muscle (Moiseenko and Kudryavtseva, 2001). The Zn concentrations found in this study were higher than those reported by Tayel (1995) in fish from the Bay of Egypt and by Lewis et al. (2002) in fish from the Gulf of Mexico. On the other hand, Ünlü et al. (1996) found higher levels of Zn (11–61 mg/kg) in grey mullet from the Tigris River (Turkey).

In order of significance, the Zn concentrations were followed by Fe (4.04–5.17 mg/kg), Mn (2.74–7.83 mg/kg) and As (1.50–2.95 mg/kg). These levels were higher than those obtained by Tariq et al. (1996) in different fish in the Indus River (Pakistan). Lewis et al. (2002) found a mean As concentration of 7.0 mg/kg in fish from the Gulf of Mexico, higher than in our study, whereas they obtained lower Fe and Mn content (2.1 and 0.07 mg/kg, respectively). The Cu concentrations obtained in this study ranged from 0.43 to 0.87 mg/kg. These values fall within the range (0.2–2.5 mg/kg) that, according to Thompson (1990), fish muscle typically contains. Finally, the least abundant metals were Hg (0.01–0.02 mg/kg) and Cd (0.01–0.03 mg/kg). These values are similar to those reported by Rayment and Barry (2000) in four fish species caught adjacent to Raine Island in northern Britain.

### 3.4. Comparison of the species

A comparison of the metal concentrations in the three species analysed (see Fig. 4) revealed the highest mean concentrations of Mn, Zn, Cu, Hg, Cd, Pb and Cr in eel muscle, while grey mullet presented the lowest mean levels of these metals.

In the livers, common sole was the species showing the lowest mean concentrations of most of the metals analysed (Hg, Zn, Ni, Cd and Pb), followed by the eel (As and Cu). On the contrary, grey mullet showed the largest number of maximum values (Hg, Zn, Ni and Cd), followed by the eel (Fe, Pb and Cr).

### 3.5. Human consumption

Spanish legislation establishes maximum levels for four of the metals studied, above which human consumption is not permitted: 1 mg/kg for Cd, 20 mg/kg for Cu, 1 mg/kg for Hg and 2 mg/kg for Pb (all expressed in wet mass) (BOE, 1991). The concentrations of these metals in muscle in the three species studied were in all cases considerably lower than the maximum levels set by law and, therefore, the muscle of all the fish analysed was fit for human consumption in Spain.

The metal with the concentration closest to the legal limit was Cu which, nonetheless, only reached levels more than 10 times below the guideline, and the furthest was Hg with concentrations over 40 times below the guideline.

There is also legislation in other countries regulating the maximum concentrations of other metals. For example, the

### Table 5

<table>
<thead>
<tr>
<th>Water</th>
<th>Sediment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Muscle Grey mullet</td>
<td>As (0.98)</td>
</tr>
<tr>
<td>Grey mullet</td>
<td>Zn (0.91)</td>
</tr>
<tr>
<td>Eel</td>
<td>As (0.91)</td>
</tr>
<tr>
<td>Common sole</td>
<td>Mn (0.94)</td>
</tr>
<tr>
<td>Liver Grey mullet</td>
<td>As (0.96)</td>
</tr>
<tr>
<td>Grey mullet</td>
<td>Mn (0.91)</td>
</tr>
<tr>
<td>Eel</td>
<td>As (0.98)</td>
</tr>
<tr>
<td>Common sole</td>
<td>As (0.94)</td>
</tr>
</tbody>
</table>

The correlation coefficient is shown in parentheses.
Western Australian Food and Drug Regulations List limits the levels for Cr and Ni at 5.5 mg/kg and 40 mg/kg for Zn (Tayel, 1995). According to the UK Food Standards Committee Report, Zn levels in food should not exceed 50 mg/kg (Cronin et al., 1998). These limits were not exceeded in the muscle of any of the fish analysed in this study. The highest concentrations found for these elements in muscle were five times lower than the legislated level for Zn, 15 for Cu and 80 for Ni. We can therefore conclude that these metals present no problem for the consumption of muscle of these fish.

In the liver, only the Cu levels were above the Spanish legal limits and occurred in the three fish species from the Odiel seawater reservoirs. Of the three, the grey mullet presented the greatest excess, with a maximum concentration eight times higher than the legal limit in the Liebre reservoir.

In relation to the other legislation mentioned above, only the Zn limit was exceeded and only in the Liebre reservoir, where the concentration was 1.5 times above the maximum UK limit.

However, fish livers are very seldom consumed except in restricted areas where the daily intake is fortunately low (Hamza-Chaffai et al., 1996).

3.6. Correlation between fish, water and sediment

Table 5 shows the metals with the highest correlation coefficients ($r > 0.90$, which means $p < 0.05$) between the concentrations in fish, water and sediment. We can see that there are more metals with high correlation coefficients between fish and water than between fish and sediment. We also note that there are more metals with high correlation coefficients in livers than in muscle, and the common sole presents the greatest number of metals with correlations between liver, water, and sediment, while the eel shows the lowest number of metals. Grey mullet and eels have the greatest number of metals with high coefficients in muscle.

From the foregoing, we can conclude that metal concentrations in the liver of some fish species can be useful as bioindicators of the degree of pollution in marine ecosystems, which is in line with the results of other research (Linde et al., 1996; Hamza-Chaffai et al., 1996; Al-Yousuf et al., 2000).

4. Conclusions

The water, sediment and fish from the Odiel seawater reservoirs (Bacuta and Liebre) showed greater concentrations of most of the metals studied than those from the Cádiz reservoirs (San Juan and San Carlos), undoubtedly because these reservoirs are affected by contamination from the Odiel River, which crosses the Iberian pyrite belt.

The metal content in fish livers was considerably higher than in muscle. We found high enrichment factors in the livers for Fe and Cu (over 100) and less for Zn, Ni, Cd and Pb (around 5).

A comparison of the species analysed showed that the grey mullet is the fish that accumulates the most metal in the liver and, on the contrary, the least in muscle. The eel shows the highest levels of metals in muscle, with average maximum concentrations of Mn, Zn, Cu, Hg, Cd, Pb and Cr.

From the legal standpoint, the muscle of all the fish caught was suitable for human consumption, although half of the fish came from a highly polluted area (the Odiel seawater reservoirs). In the liver (viscera not usually consumed), the maximum legal limit of Cu permitted by Spanish legislation was exceeded in all three species caught in the Odiel seawater reservoirs.

Among the species studied, the common sole was the most suitable for use as a bioindicator of pollution, particularly its liver. We found the largest number of significant correlations between the metal content in the liver of common sole and the water content, and between the contents in liver and sediment.

References


BOE (Boletín Oficial del Estado or Official Gazette). Normas microbiológicas, límites de contenido en metales pesados y métodos analíticos para la determinación de metales pesados para los productos de la pesca y de la agricultura (Microbiological standards, limits on heavy metal content, and analytical methods for determining the heavy metal content of fishery and agricultural products). In: BOE, editors. August 2 Order. Madrid, Spain; 1991. p. 5937–41.


Karadede H, Ünlü E. Concentrations of some heavy metals in water, sediment and fish species from the Atatürk Dam Lake (Euphrates), Turkey. Chemosphere 2000;41:1371–6.


Kucukseven F, Altay O, Uluturhan E, Kontas A. Trace metal and organochlorine residue levels in red mullet (Mullus barbatus) from the Eastern Aegean, Turkey. Water Res 2001;35(9):2327–32.


Miao XS, Woodward LA, Swenson C, Li QX. Comparative concentrations of some heavy metals in water, sediment, benthic invertebrates, and tissues of white sucker (Fundulus hepatus) and mullet (Liza anguilla) in some brackish waters of Sunderban, India. Mar Pollut Bull 2000;40(11):914–20.


Miller PA, Murray RR, Dixon DG. Relationship between concentrations of copper and zinc in water, sediment, benthic invertebrates, and tissues of white sucker (Catostomus commersonii) at metal-contaminated sites. Can J Fish Aquat Sci 1992;49:978–85.


Moisenko TI, Kudryavtseva LP. Trace metal accumulation and fish pathologies in areas affected by mining and metallurgical enterprises in the Kola Region, Russia. Environ Pollut 2001;114:285–97.